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PUBLICATIONS

Review Articles

1. *Nonadiabatic Interactions Between Potential Energy Surfaces: Theory and Applications*
B. H. Lengsfeld and D. R. Yarkony, *Advances in Chemical Physics: State-Selected and State to State Ion-Molecule Reaction Dynamics: Theory, Part II*, eds. C. Y. Ng and M. Baer, (John Wiley and Sons, New York, 1992), vol 82.
2. *Spin-forbidden Chemistry Within the Breit-Pauli Approximation*
D. R. Yarkony, *Int. Reviews of Phys. Chem.* **11**, 195 (1992).

Journal Articles

1. On the Noncrossing Rule in Polyatomic Systems: Determination of a Seam of Actual Surface Crossings Relevant to the Quenching of $H_2(B^1\Sigma_u^+)$ by Helium
M. R. Manaa and D. R. Yarkony, *J. Chem. Phys.* **93**, 4473 (1990)
2. Spin-Forbidden Decay of the Dication HS^{2+}
Gérard Parlant, Jörg Senekowitsch, Stephen V. O'Neil, David R. Yarkony, *J. Chem. Phys.*, **94**, 7208 (1991).
3. On the Mechanism of the Reaction $CH(X^2\Pi) + N_2(X^1\Sigma_g^+) \rightarrow HCN(X^1\Sigma^+) + N(^4S)$. I: A Theoretical Treatment of the Electronic Structure Aspects of the Intersystem Crossing
M. Riad Manaa and David R. Yarkony, *J. Chem. Phys.*, **95**, 1808 (1991)

5. A Theoretical Treatment of the $a^3\Sigma_1^+ \rightarrow X^1\Sigma_0^+$ Spin-Forbidden Dipole-Allowed Radiative Transition in NO^+
M. Riad Manaa and David R. Yarkony, J. Chem. Phys., 95, 6562 (1991)
6. On the Mechanism of the Reaction $\text{CH}(X^2\Pi) + \text{N}_2(X^1\Sigma_g^+) \rightarrow \text{HCN}(X^1\Sigma^+) + \text{N}(^4\text{S})$. II: The Intermediate Complex Region,
M. Riad Manaa and David R. Yarkony, Chem. Phys. Lett., 188, 352 (1992).
7. Theoretical Studies of Spin-Forbidden Radiationless Decay in Polyatomic Systems: Insights from Recently Developed Computational Methods
David R. Yarkony, J. Amer. Chem. Soc., 114, 5406, (1992)
8. On the Intersection of Potential Energy Surfaces in Charge Transfer Reactions: A Crossing Seam for Two States of the Same Symmetry in the Reaction $\text{H}^+ + \text{NO}(X^2\Pi) \rightarrow \text{H} + \text{NO}^+(X^1\Sigma^+)$
M. R. Manaa and D. R. Yarkony, J. Chem. Phys., 97, 715 (1992).
9. Theoretical Studies of Spin-Forbidden Radiationless Decay in Polyatomic Systems II: Radiationless Decay of $a\text{-N}_2\text{O}_2$
Kiet A. Nguyen, Mark S. Gordon, John A. Montgomery, Jr., H. Harvey Michels and David R. Yarkony, J. Chem. Phys. (March 1993)

ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS

This research program focusses on the electronic structure aspects of radiationless decay processes related to the stability and formation of high energy density materials. We have also begun theoretical studies on electronic nonadiabaticity in ion-molecule reactions. These studies are enabled by a unique system of electronic structure algorithms, the BROOKLYN programs, which we have developed over the last decade. These programs provide advanced capabilities for the study of the electronic structure aspects of spin-forbidden and spin-allowed electronically nonadiabatic processes. The methodology we have developed is based *exclusively* on large scale configuration state function expansions (10^5 – 10^6 terms). These methods, which we believe *define* the state of the art in these areas, have permitted us to make significant contributions to the understanding of electronically nonadiabatic processes. Problems of particular relevance to the high energy density materials program include studies of the stability of the potential energetic species $a\text{-N}_2\text{O}_2$, tetrahedral N_4 and the dication HS^{2+} . We have also initiated a research program in ion-molecule chemistry reporting for the first time a seam of crossings of two states of the *same symmetry* for the prototypical charge transfer reaction $\text{H}^+ + \text{NO} \rightarrow \text{H} + \text{NO}^+$.

Finally a new phase of program development has been initiated with the goal of extending our capabilities for the direct determination of actual/allowed/avoided crossing hyperlines and hyperplanes. The algorithms under development will permit systematic determination of (i) actual/allowed crossing seams passing through a minimum energy crossing point and (ii) avoided crossing seams as a function of an arbitrary set of internal coordinates. This program development, which will be completed during our present AFOSR sponsored research program, will provide powerful new tools for the study of spin-forbidden and spin-allowed electronically nonadiabatic processes in polyatomic systems.

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REPORT DEFINITION

GRANT:	AFOSR-90-0051
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SUMMARY

This research program focusses on the electronic structure aspects of radiationless decay processes related to the stability and formation of high energy density materials. We have also begun theoretical studies on electronic nonadiabaticity in ion-molecule reactions. These studies are enabled by a unique system of electronic structure algorithms, the BROOKLYN programs, which we have developed over the last decade. These programs provide advanced capabilities for the study of the electronic structure aspects of spin-forbidden and spin-allowed electronically nonadiabatic processes. The methodology we have developed is based *exclusively* on large scale configuration state function expansions (10^5 – 10^6 terms). These methods, which we believe *define* the state of the art in these areas, have permitted us to make significant contributions to the understanding of electronically nonadiabatic processes. Problems of particular relevance to the high energy density materials program include studies of the stability of the potential energetic species α -N₂O₂, tetrahedral N₄ and the dication HS²⁺. We have also initiated a research program in ion-molecule chemistry reporting for the first time a seam of crossings of two states of the *same symmetry* for the prototypical charge transfer reaction $H^+ + NO \rightarrow H + NO^+$.

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TECHNICAL REPORT

One of the principal aspects of our research program has been the development of new theoretical tools for treating spin-forbidden and spin-allowed electronically nonadiabatic processes. These tools have then been used to study, the stability and/or decay mechanisms of potential high energy density materials(HEDM's) and, ion-molecule chemistry. We believe that as a result of computational limitations the electronic structure aspects of these important classes of chemical problems had received inadequate treatment. The methodology we developed is based *exclusively* on large scale configuration state function expansions (10^5 – 10^6 terms). These methods, which we believe *define* the state of the art in these areas, have permitted us to make significant contributions to the understanding of radiationless decay processes and electronically nonadiabatic chemical reactions. Below we outline the methods we have developed and their applications in the HEDM and ion-molecule chemistry programs.

I: METHODS: SPIN-FORBIDDEN PROCESSES

Our studies in the area of spin-forbidden chemistry employ the Breit-Pauli approximation¹ and consider those interactions which lift the $2S+1$ degeneracy associated with the total electron spin quantum number, S . These interactions are the full microscopic spin-orbit interaction H^{so} :

$$H^{so} = \sum_{i=1}^N \mathbf{h}^{so}(i) \cdot \mathbf{s}_i + \sum_{i,j=1}^N \mathbf{h}^{soo}(i,j) \cdot (\mathbf{s}_i + 2\mathbf{s}_j) \quad 1.1$$

and the dipolar spin-spin interaction H^{ss}

$$H^{ss} = \sum_{i,j=1}^N \mathbf{s}_i \cdot \mathbf{h}^{ss}(i,j) \cdot \mathbf{s}_j \quad 1.2$$

where $\mathbf{h}^{so}(i)$, $\mathbf{h}^{soo}(i,j)$, and $\mathbf{h}^{ss}(i,j)$ are the microscopic spin-orbit, spin-other-orbit, and dipolar spin-spin interactions¹ and we write $H^{BP} = H^{so} + H^{ss}$.

(A) Methodology

Our treatment of these interactions is *unique in two* ways. We use the symbolic matrix element methods originally introduced in the treatment of the nonrelativistic Born Oppenheimer hamiltonian H^0 by Liu and Yoshimine² to evaluate the matrix elements of H^{so} ³ and H^{ss} ⁴ in the N -electron configuration state function (CSF) space. This enables the use of large scale CSF spaces

(10^5 – 10^6 terms) to characterize these interactions. These spaces are one to two orders of magnitude larger than those accessible using previously existing methods^{5,6} and this capability has improved significantly the reliability of theoretical work in this area.

The second unique aspect of our approach involves the manner in which the relativistic wavefunction is obtained from the zeroth order nonrelativistic [configuration interaction (CI)] wavefunction^{7,8} Within the context of the Breit-Pauli approximation the relativistic wavefunction, $\Psi(I)$, is obtained from the zeroth order nonrelativistic wavefunction, $\Psi^0(I)$, using perturbation theory. In order to allow for the possibility of intersections or near intersections of potential energy surfaces we have developed an approach based on quasi-degenerate perturbation theory. The description which emerges from this formalism expresses the electronic wavefunctions as a linear combination of dressed diabatic wavefunctions [$\Psi^d(I)$]

$$\Psi^d(I) = \Psi^0(I) + \Psi_Q^{1,d}(I) \quad 1.3$$

where $\Psi^0(K)$ satisfies the nonrelativistic Schrödinger equation

$$[H^0 - E^0(I)]\Psi^0(I) = 0 \quad 1.4$$

and the dressing term, $\Psi_Q^{1,d}(I)$ represents the perturbation of the (diabatic) quasidegenerate state $\Psi^0(I)$ by states *outside* the quasidegenerate space and satisfies

$$[H^0 - E^0(I)]\Psi_Q^{1,d}(I) = -QH^{BP}\Psi^0(I) \quad 1.5$$

where Q projects onto the orthogonal complement of the quasidegenerate space. The quasidegenerate dressed diabatic states $\Psi^d(I)$, the analogues of the $\Psi^0(I)$ in eq. 1.4, are mixed by the Breit-Pauli interaction H^{BP} . This mixing is given by a secular equation with the dimension of the quasidegenerate space and having the form:

$$\begin{pmatrix} H_{1,1} - E & H_{1,2} & \dots & H_{1,M} \\ \vdots & H_{2,2} - E & & \\ H_{M,1} & & \ddots & H_{M,M} - E \end{pmatrix} \begin{pmatrix} \Psi^d(1) \\ \vdots \\ \Psi^d(M) \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ \vdots \\ 0 \end{pmatrix} \quad 1.6$$

where $H_{I,J} = \langle \Psi^d(I) | H^0 + H^{BP} | \Psi^d(J) \rangle$. Since the coupling between the states $\Psi^d(I)$ originates from a potential term H^{BP} rather than the derivative coupling terms, to be discussed subsequently, the $\Psi^d(I)$ are referred to as diabatic states.

This approach is distinguished from the commonly used approach⁹ in which eq. 1.5 is replaced with a spectral expansion of $\Psi_Q^{1,d}(I)$

$$\Psi_Q^{1,d}(I) = \sum_{K \in Q} \frac{\langle \Psi^0(K) | H^{BP} \Psi^0(I) \rangle}{E^0(K) - E^0(I)} \Psi^0(K) \quad 1.7$$

This procedure is unsatisfactory owing to the need to drastically truncate the sum in eq. 1.7. The use of eq. 1.5 in lieu of eq. 1.7 has improved considerably our ability to predict rates for spin-forbidden dipole-allowed radiative decay processes.

II: NONADIABATIC PROCESSES

A: Determination of Seams of Avoided/Actual Crossings Seams Using Analytic Derivative Techniques

When considering the stability of energetic local extrema on the ground potential energy surface one must consider the possibility of interactions with nominally excited potential energy surfaces as these interactions may lead to dissociation channels for the metastable energetic species. Yet in the absence of simplifications attributable spacial symmetry such regions of nuclear coordinate space are difficult to isolate. On the basis of these simple observations rests the need for an algorithm for the determination of regions of close approach of two potential energy surfaces. Regions of close approach can be classified as actual/allowed/avoided surface crossings. Actual (allowed) surface crossings represent the intersection of two potential energy surfaces of the same (different) symmetry. The set of all such points forms a surface of dimension $N-2$ ($N-1$) where N is the number of internal nuclear degrees of freedom. Actual crossing are permitted by the multidimensional breakdown of the vonNeumann-Wigner noncrossing rule.¹⁰ Since the multidimensional breakdown of the noncrossing rule *permits but does not guarantee* the existence of actual crossings, actual crossing seams can merge smoothly into avoided crossing seams of the same dimension. Our capability for the determination of seams of avoided/actual surface crossings rests on an isomorphism connecting the equations used in constructing energy gradients, energy difference gradients and the (CI contribution) to the first

derivative nonadiabatic coupling matrix elements.¹¹ The essential elements of this isomorphism are outlined below.

We are required to construct a generalized first derivative with respect to the internal coordinate R_α . This quantity has the form

$$q_\alpha^{IJ}(\mathbf{R}) = Q_{IJ}^\alpha(\mathbf{R}) + Q_{IJ}^{U\alpha}(\mathbf{R}) \quad 2.1$$

where the first term gives the contribution attributable to changes in the atomic orbital integrals

$$Q_{IJ}^\alpha = \sum_{i,j} \rho_{ij}^{IJ} h_{ij}^\alpha + \sum_{i,j,k,l} P_{ijkl}^{IJ} (ij || kl)^\alpha \quad 2.2$$

and the second term gives the contribution attributable to changes in the molecular orbitals

$$Q_{IJ}^{U\alpha} = \sum_{i,j} L_{ij}^{IJ} U_{ij}^\alpha \quad 2.3$$

Here ρ_{ij}^{IJ} and P_{ijkl}^{IJ} , defined further below, are generalized one and two particle density matrices for multireference CI wavefunctions $\Psi^0(I)$ and $\Psi^0(J)$ and the generalized Lagrangian L^{IJ} is given by

$$L_{im}^{IJ} = 2 \left[\sum_j \rho_{ij}^{IJ} h_{mj} + 2 \sum_{j,k,l} P_{ijkl}^{IJ} (mj || kl) \right] \quad 2.4$$

In the above h^α and $(ij||kl)^\alpha$ are the derivatives of the standard one and two electron integrals with respect to R_α , and the $U^\alpha(\mathbf{R})$ represent the derivatives of the molecular orbital coefficients, that is

$$\frac{\partial}{\partial R_\alpha} \phi_i(r; \mathbf{R}) = \sum_j \phi_j(r; \mathbf{R}) U_{ji}^\alpha + \sum_j \left[\frac{\partial}{\partial R_\alpha} \chi_j(r; \mathbf{R}) \right] t_{ji}(\mathbf{R}) \quad 2.5$$

where $\phi(r; \mathbf{R})$ [$\chi(r; \mathbf{R})$] are the molecular (atomic) orbitals and $t(\mathbf{R})$ expresses the molecular orbitals in terms of the atomic orbital basis. The $U^\alpha(\mathbf{R})$ are determined from the coupled perturbed state averaged MCSCF equations.^{12, 13, 14}

Eqs. 2.1–2.4 constitute the aforementioned isomorphism. The desired derivative quantities are obtained by replacing the general density matrices ρ and P with specific density matrices as given below:

(a) Energy Gradient $\frac{\partial}{\partial R_\alpha} E^I(\mathbf{R})$: standard density matrices^{15, 16}

$$\rho_{ij}^{IJ} \rightarrow \gamma_{ij}^{II} \text{ and } P_{ijkl}^{IJ} \rightarrow \Gamma_{ijkl}^{II}$$

$$q_{\alpha}^{IJ}(\mathbf{R}) \rightarrow \frac{\partial}{\partial R_{\alpha}} E^I(\mathbf{R}) - \frac{\partial}{\partial R_{\alpha}} V^N(\mathbf{R}) ;$$

(b) Energy Difference Gradient $\frac{\partial}{\partial R_{\alpha}} \Delta E^{IJ}(\mathbf{R})$: difference density matrices

$$\rho_{ij}^{IJ} \rightarrow \gamma_{ij}^{II} - \gamma_{ij}^{JJ} \text{ and } P_{ijkl}^{IJ} \rightarrow \Gamma_{ijkl}^{II} - \Gamma_{ijkl}^{JJ}$$

$$q_{\alpha}^{IJ}(\mathbf{R}) \rightarrow \frac{\partial}{\partial R_{\alpha}} \Delta E^{IJ}(\mathbf{R}) \equiv g_{\alpha}^{IJ}(\mathbf{R})$$

where $\Delta E^{IJ}(\mathbf{R}) = E_I(\mathbf{R}) - E_J(\mathbf{R})$; and

(c) Derivative Couplings $\left\langle \Psi_i^0(\mathbf{r}; \mathbf{R}) \left| \frac{\partial}{\partial R_{\alpha}} \Psi_j^0(\mathbf{r}; \mathbf{R}) \right\rangle_r$: transition density matrices

$$\rho_{ij}^{IJ} \rightarrow \gamma_{ij}^{IJ} \text{ and } P_{ijkl}^{IJ} \rightarrow \Gamma_{ijkl}^{IJ},$$

$$q_{\alpha}^{IJ}(\mathbf{R}) / \Delta E^{IJ}(\mathbf{R}) \rightarrow {}^{CI}f_{\alpha}^{IJ}(\mathbf{R})$$

with the complete first derivative nonadiabatic coupling matrix element $f_{\alpha}^{IJ}(\mathbf{R}) =$

$$\left\langle \Psi_i^0(\mathbf{r}; \mathbf{R}) \left| \frac{\partial}{\partial R_{\alpha}} \Psi_j^0(\mathbf{r}; \mathbf{R}) \right\rangle_r \text{ given by: }^{13, 17}$$

$$f_{\alpha}^{IJ}(\mathbf{R}) \equiv {}^{CI}f_{\alpha}^{IJ}(\mathbf{R}) + {}^{CSF}f_{\alpha}^{IJ}(\mathbf{R}) \quad 2.6$$

where

$${}^{CSF}f_{\alpha}^{IJ}(\mathbf{R}) \equiv \sum_{i,j} \gamma_{ij}^{IJ} d_{ij}^{\alpha}(\mathbf{R}) \quad 2.7$$

and

$$d_{ij}^{\alpha}(\mathbf{R}) \equiv \left\langle \phi_i(\mathbf{r}; \mathbf{R}) \left| \frac{\partial}{\partial R_{\alpha}} \phi_j(\mathbf{r}; \mathbf{R}) \right\rangle \quad 2.8$$

The antisymmetric matrix $\mathbf{d}^{\alpha}(\mathbf{R})$ is readily determined from eq. 2.5 once the $\mathbf{U}^{\alpha}(\mathbf{R})$ are available.

The direct determination of the energy difference gradient is the key to our algorithm for the efficient determination of actual/avoided surface crossings.¹¹ This intersurface feature is obtained by minimizing $\Delta E^{IJ}(\mathbf{R})^2$ using a Newton-Raphson procedure. The requirement that $\Delta E^{IJ}(\mathbf{R})^2$ be a minimum yields:

$$\frac{\partial}{\partial R_{\alpha}} \Delta E^{IJ}(\mathbf{R})^2 = 2 \Delta E^{IJ}(\mathbf{R}) g_{\alpha}^{IJ}(\mathbf{R}) = 0 \quad 2.9$$

Eq. 2.9 shows that both avoided and actual surface crossings can be obtained from the same algorithm and evinces the role of the energy difference gradient in such a procedure.

B: Determination of the Minimum Energy Crossing Point on the Surface of Intersection of Two States of Different Spin-Multiplicity Using Analytic Derivative Techniques

When considering a nonadiabatic processes involving states of different spin-multiplicity one is only concerned with allowed surface crossings. The minimum energy point on the surface of intersections represents a key bottleneck along the minimum energy path in a spin-forbidden process and frequently represents the barrier for this process. Thus the direct characterization of this point is an essential first step in any treatment of a spin-forbidden electronically nonadiabatic process.

The straightforward procedure that has been used in the past to locate the minimum energy point,¹⁸ the indirect determination of this point, initially determines the crossing surface and then characterizes its minimum. This procedure is computationally costly since for a system with N internal degrees of freedom a crossing subsurface, or hyperplane, of dimension $N-1$ must be determined and analyzed. Thus the determination of this point represents a significant computational bottleneck. However this bottleneck can be avoided. The minimum energy crossing point can be determined directly, that is without prior determination of the surface of intersection itself, using a Lagrange-Newton procedure¹⁹ which minimizes the quantity

$$L_{JI}(\mathbf{R}, \lambda) = E_I^0(\mathbf{R}) + \lambda[E_J^0(\mathbf{R}) - E_I^0(\mathbf{R})] \quad 2.10a$$

$$= E_I^0(\mathbf{R}) + \lambda \Delta E^{JI}(\mathbf{R}) \quad 2.10b$$

where \mathbf{R} denotes the nuclear coordinates and λ is a Lagrange multiplier. Expanding eq. 2.10 to second order yields the Lagrange-Newton equations^{11, 19, 20}

$$\begin{pmatrix} \mathbf{W}(\mathbf{R}, \lambda) & \mathbf{g}''(\mathbf{R}) \\ \mathbf{g}''(\mathbf{R})^\dagger & 0 \end{pmatrix} \begin{pmatrix} \delta \mathbf{R} \\ \delta \lambda \end{pmatrix} = - \begin{pmatrix} \mathbf{g}'(\mathbf{R}) + \lambda \mathbf{g}''(\mathbf{R}) \\ \Delta E''(\mathbf{R}) \end{pmatrix} \quad 2.11$$

where $\delta \mathbf{R} = \mathbf{R}' - \mathbf{R}$, $\delta \lambda = \lambda' - \lambda$,

$$W_{\alpha\beta}''(\mathbf{R}, \lambda) = \frac{\partial^2 L_{JI}(\mathbf{R}, \lambda)}{\partial R_\alpha \partial R_\beta} = \frac{\partial}{\partial R_\alpha} [\mathbf{g}'_\beta(\mathbf{R}) + \lambda \mathbf{g}''_\beta(\mathbf{R})] \quad 2.12$$

and the gradients are defined as

$$g_a''(\mathbf{R}) = g_a'(\mathbf{R}) - g_a'(\mathbf{R}) = \frac{\partial \Delta E_{JI}(\mathbf{R})}{\partial R_a} \quad 2.13a$$

and

$$g_a'(\mathbf{R}) = \frac{\partial E_f^0(\mathbf{R})}{\partial R_a} \quad 2.13b$$

We have implemented an algorithm for the solution of eq. 2.11 in which the gradients, eq. 2.13, are evaluated, for MCSCF/CI wavefunctions, using analytic derivative techniques (eqs. 2.1-2.4).^{11, 21} $W_{\alpha\beta}^{IJ}(\mathbf{R}, \lambda)$ is determined using a forward or a centered difference of $g_{\beta}^I + \lambda g_{\beta}^{IJ}$, that is:

$$W_{\alpha\beta}^{IJ}(\mathbf{R}, \lambda) = \left\{ \left[g_{\beta}^I(\mathbf{R} + \epsilon \mathbf{I}^{\alpha}) + \lambda g_{\beta}^{IJ}(\mathbf{R} + \epsilon \mathbf{I}^{\alpha}) \right] - \left[g_{\beta}^I(\mathbf{R}) + \lambda g_{\beta}^{IJ}(\mathbf{R}) \right] \right\} / \epsilon \quad 2.14a$$

or

$$= \left\{ \left[g_{\beta}^I(\mathbf{R} + \epsilon \mathbf{I}^{\alpha}) + \lambda g_{\beta}^{IJ}(\mathbf{R} + \epsilon \mathbf{I}^{\alpha}) \right] - \left[g_{\beta}^I(\mathbf{R} - \epsilon \mathbf{I}^{\alpha}) + \lambda g_{\beta}^{IJ}(\mathbf{R} - \epsilon \mathbf{I}^{\alpha}) \right] \right\} / 2\epsilon \quad 2.14b$$

where \mathbf{I}^{α} is a unit vector along the direction R_{α} .

The use of analytic gradient techniques permits the solution of eq. 2.11 in the *full* nuclear coordinate space. An analysis of the nuclear configuration and wavefunctions at the minimum energy crossing point can provide valuable mechanistic insights into a spin-forbidden reaction.²¹⁻²³

III. APPLICATIONS

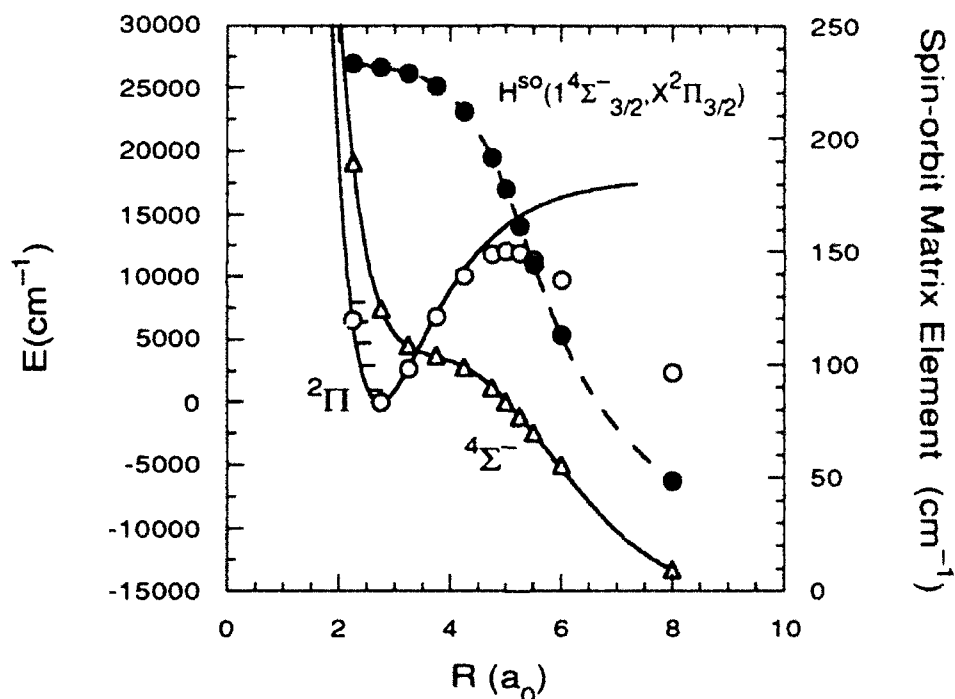
A. High Energy Density Materials

(i): Stability of Dications with Respect to Spin-Forbidden Radiative Decay

In a recent combined theoretical/experimental study at the University of Colorado at Boulder Miller *et al.*²⁴ reported the existence of the dication HS^{2+} . The vibrational levels of the state observed, the $X^2\Pi$ electronic state, must be metastable with a lifetime greater than 10 μsec to be detected in their experiment. Using large scale complete active space(CAS)²⁵⁻²⁷/configuration interaction(CI) wavefunctions these authors determined the potential energy curve for the $X^2\Pi$ state (see figure below). They showed that the barrier in the $X^2\Pi$ potential energy curve, attributable to an avoided crossing between $^2\Pi$ states correlating with H^+S^+ and HS^{2+} , can support eight quasibound vibrational levels. Tunneling on the $X^2\Pi$ potential energy curve limits the lifetime of the vibrational levels with $v \geq 5$ to 100 μsec or less. However these authors also

determined that a dissociative $4\Sigma^-$ electronic state crosses the bound $X^2\Pi$ state at $R=1.81\text{ \AA}$ ($3.42a_0$) at an energy above that of $X^2\Pi$, $v=1$ level. This crossing provides an additional decay channel for the vibrational levels of the $X^2\Pi$ state resulting from the spin-orbit perturbation $X^2\Pi \sim 1^4\Sigma^-$.

As part of collaboration with the Boulder group we undertook a study of the efficacy of this mechanism using a combination of *ab initio* electronic structure, and coupled state nuclear dynamics, calculations. The following figure summarizes the results of our *ab initio* calculations which determined both the potential energy curves for the $X^2\Pi$ and $1^4\Sigma^-$ states as well as the requisite spin-orbit coupling $H^{so}(1^4\Sigma^-_X, X^2\Pi_\Omega) \equiv \langle \Psi(1^4\Sigma^-_\Omega) | H^{so} | \Psi(X^2\Pi_\Omega) \rangle$.



Using this data the radiationless decay lifetimes were determined within a Hund's case (a) approximation. The most important conclusion of this study is that the $1^4\Sigma^- \sim X^2\Pi$ state interaction significantly shortens the single state tunneling lifetimes of the vibrational levels of the $X^2\Pi$ state reported by Miller *et al.* Despite the fact that the radiationless decay of the $v=0, 1$

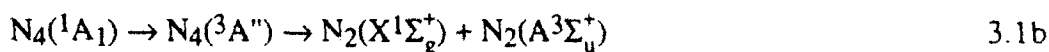
levels is due to spin-orbit induced tunneling we find that only the $v=0$ level will be observable on the time scale of the above noted experiment.

(ii): Spin-forbidden Radiationless Decay in Tetrahedral N_4 .

The potential energetic material tetrahedral N_4 ²⁸ has been the subject of several recent high quality theoretical studies^{28, 29, 30} that have demonstrated that this species is in fact a local minimum on the lowest $^1A'$ potential energy surface. However this species has yet to be synthesized. The barrier to spin-allowed decay of N_4



is approximately 61kcal/mol.³⁰ It has been suggested³⁰ that the spin-forbidden decay channel



limits the lifetime of tetrahedral N_4 and is therefore responsible for the inability to synthesize this species.

The decay channel given by eq. 3.1b had not been previously investigated. Our treatment of this system²¹ found, using eq. 2.11 and multireference CI expansions with over 400,000 terms, that the minimum energy crossing point of the $^1A'$ and $^3A''$ potential energy surfaces is only 28kcal/mol above the 1A_1 minimum on the $^1A'$ potential energy surface corresponding to tetrahedral N_4 ! This important finding means that, (i) the lowest vibrational levels of N_4 are unlikely to be predissociated by this mechanism, and (ii) spin-forbidden radiative decay must be considered in any realistic treatment of the lifetime of tetrahedral N_4 . We intend to pursue this point further using a golden rule wavepacket method for determining the radiationless decay rate.³¹ This method should be computationally tractable for a polyatomic system since the wavepacket need only be propagated for a short time on the dissociative surface.³¹

(iii): On the Stability of α - N_2O_2

The asymmetric dimer of NO, α - N_2O_2 , had previously been suggested by Michels and Montgomery as a potential energetic material.³² In collaboration with Mark Gordon's group at Iowa State University and Michels and Montgomery the stability of this system with respect to the exoergic but spin-forbidden radiationless decay process



was considered. Large scale multireference configuration interaction wavefunctions, comprised of approximately 300,000 – 1,400,000 configuration state functions, based on double zeta polarization and triplet zeta polarization bases were used to study this process. The minimum energy crossing of the ground singlet $^1\text{A}'$, and the lowest excited triplet $^3\text{A}''$, potential energy surfaces was determined as was the interstate spin-orbit coupling.

$a\text{-N}_2\text{O}_2$ is perhaps best described as $\text{O}(^1\text{D})$ datively bound to $\text{N}_2\text{O}(\text{X}^1\Sigma^+)$. A low-lying triplet state correlating with $\text{N}_2\text{O}(\text{X}^1\Sigma^+) + \text{O}(^3\text{P})$ was found to intersect (at a geometrical arrangement labelled MEX) the $^1\text{A}'$ potential energy surface only 1.0 – 2.0 kcal/mol above the $a\text{-N}_2\text{O}_2$ equilibrium structure, denoted $\text{MIN}(^1\text{A}')$. $\text{MIN}(^1\text{A}')$ and MEX differ only in $\text{R}(\text{O}^1\text{--O}^2)$ which increases by 0.12 Å going from $\text{MIN}(^1\text{A}')$ to MEX. The spin-orbit coupling H_{\parallel}^{so} was found to be large in this region, $H_{\parallel}^{so} \sim 75\text{cm}^{-1}$. The structural similarity among $\text{MIN}(^1\text{A}')$, MEX and isolated $\text{N}_2\text{O}(\text{X}^1\Sigma^+)$ permits the spin-forbidden predissociation to be studied using a simple one-dimensional model. This model predicts that $a\text{-N}_2\text{O}_2$ will be rapidly (on the order of picoseconds) dissociated to $\text{N}_2\text{O}(\text{X}^1\Sigma^+)$ and $\text{O}(^3\text{P})$ as in eq. 3.2 and thus is NOT a HEDM candidate.

B. Ion-Molecule Chemistry

The charge transfer reaction,^{33, 34} $\text{B}^+ + \text{A} \rightarrow \text{B} + \text{A}^+$, is perhaps the archetypical example of an electronically nonadiabatic process³⁵ involving a transition between the electronic potential energy surfaces corresponding to $\text{B}^+ + \text{A}$ and $\text{B} + \text{A}^+$. Such processes play an important role in the chemistry of the upper atmosphere.

(i): Actual/Allowed Crossing Seams in the Reaction $\text{H}^+ + \text{NO} \rightarrow \text{H} + \text{NO}^+$

The location of the nuclear configurations for which the potential energy surfaces are in close proximity is of prime importance in elucidating the mechanism of a charge transfer process. In the frequently studied charge exchange systems $(\text{ArH}_2)^+$ and $(\text{ArN}_2)^+$ (Ref.36) the regions of close approach are characterized by *symmetry allowed* surface crossings of the relevant potential energy surfaces. Here symmetry allowed, or just allowed, surface crossings refer to crossings of *adiabatic* electronic states of different symmetry. Crossings of potential energy surfaces

corresponding to adiabatic electronic states of the same symmetry are normally considered rare and are usually ignored in discussions of charge transfer phenomena. Actual crossing seams are difficult to locate because they represent surfaces of intersection of dimension $N-2$ whereas for allowed crossings the surfaces of intersection are of dimension $N-1$. In fact it was not until 1990 that instances of actual crossing seams based on MCSCF (for O_3)³⁷ and MCSCF/CI (for $He-H_2$)³⁸ wavefunctions were reported. These examples had been the only reported instances of actual crossing seams based on MCSCF/CI wavefunctions. No examples of actual crossing seams relevant to charge transfer reactions existed despite the long history of theoretical studies of this class of processes.³⁴

In our initial study of the prototypical charge transfer system, HNO^+ , an actual crossing seam of two potential energy surfaces of the same symmetry relevant to the charge transfer reaction $H^+ + NO(X^2\Pi) \rightarrow H(^2S) + NO^+(X^1\Sigma^+)$ was located.³⁹ This crossing seam, $R(R) \equiv [R, r(R), \gamma(R)]$ occurs for general C_s geometries. It represents the intersection of the $1,2^2A'$ potential energy surfaces which correlate asymptotically with $H(^2S) + NO^+(X^1\Sigma^+)$ and $H^+ + NO(X^2\Pi)$ respectively. For $R \sim 2.45-3.65a_0$ the seam is exoergic relative to the reactant channel asymptote, $H^+ + NO(X^2\Pi)$. The present results complement a previous⁴⁰ determination of two *allowed* crossing seams in $C_{\infty v}$ symmetry. Thus these results provide, for the first time, an example of (i) an actual (as opposed to an allowed) crossing seam for a charge transfer reaction and (ii) a system for which *both* allowed and actual - energetically accessible - conical intersections exist. The actual crossing seam occurs for geometrical configurations in which H^+ approaches NO approximately perpendicular to the NO internuclear axis. These configurations are quite distinct from the previously determined allowed crossing seams which correspond to collinear approach. Thus these results are expected to have important implications for the energy redistribution which accompanies charge transfer. The incorporation of this actual crossing seam into any set of potential energy surfaces used to describe the charge transfer process appears essential. It will be quite interesting to see whether this feature is to be found in other charge transfer reactions.

IV. FUTURE DIRECTIONS

The research completed during the course of this grant has suggested the need for additional methods development and applications. These future research directions are indicated below. The question of spin-forbidden radiationless decay in energetic species appears to be a fairly general one. The methodology developed as part of this grant for the direct determination of the minimum energy crossing point can provide considerable insight into the feasibility of a spin-forbidden process, particularly when this point turns out to be the barrier for this process. However to enable studies of the dynamics of these processes or when the barrier does not correspond to the minimum energy crossing point it is necessary to determine more of the crossing hypersurface. To this end a new phase of program development has been initiated with the goal of extending our capabilities for the direct determination of actual/allowed/avoided crossing hyperlines and hyperplanes. The algorithms under development will permit systematic determination of (i) actual/allowed crossing seams passing through a minimum energy crossing point and (ii) avoided crossing seams parametrized by an arbitrary set of internal coordinates. This program development, to be completed during our present AFOSR sponsored research program, will provide powerful new tools for the study of spin-forbidden and spin-allowed electronically nonadiabatic processes in polyatomic systems.

Recent theoretical work in other laboratories serves to motivate applications of the methods developed in our research program. Sophisticated theoretical methods have suggested the existence of additional metastable geometrical isomers of NO dimer^{41, 42} and a metastable dication of O₄⁴³ (isoelectronic with N₂O₂) has also been predicted. It will be important to learn whether spin-forbidden radiationless decay plays a significant role in limiting the lifetime of these species.

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PUBLICATIONS

Review Articles

1. *Nonadiabatic Interactions Between Potential Energy Surfaces: Theory and Applications*
B. H. Lengsfeld and D. R. Yarkony, *Advances in Chemical Physics: State-Selected and State to State Ion-Molecule Reaction Dynamics: Theory, Part II*, eds. C. Y. Ng and M. Baer, (John Wiley and Sons, New York, 1992), vol 82.
2. *Spin-forbidden Chemistry Within the Breit-Pauli Approximation*
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Journal Articles

2. On the Noncrossing Rule in Polyatomic Systems: Determination of a Seam of Actual Surface Crossings Relevant to the Quenching of $\text{H}_2(\text{B}^1\Sigma_u^+)$ by Helium
M. R. Manaa and D. R. Yarkony, *J. Chem. Phys.* **93**, 4473 (1990)
3. Spin-Forbidden Decay of the Dication HS^{2+}
Gérard Parlant, Jörg Senekowitsch, Stephen V. O'Neil, David R. Yarkony, *J. Chem. Phys.*, **94**, 7208 (1991).
4. On the Mechanism of the Reaction $\text{CH}(\text{X}^2\Pi) + \text{N}_2(\text{X}^1\Sigma_g^+) \rightarrow \text{HCN}(\text{X}^1\Sigma^+) + \text{N}(^4\text{S})$. I: A Theoretical Treatment of the Electronic Structure Aspects of the Intersystem Crossing
M. Riad Manaa and David R. Yarkony, *J. Chem. Phys.*, **95**, 1808 (1991)
5. A Theoretical Treatment of the $\text{a}^3\Sigma_1^+ \rightarrow \text{X}^1\Sigma_0^+$ Spin-Forbidden Dipole-Allowed Radiative Transition in NO^+
M. Riad Manaa and David R. Yarkony, *J. Chem. Phys.*, **95**, 6562 (1991)
- †6. On the Mechanism of the Reaction $\text{CH}(\text{X}^2\Pi) + \text{N}_2(\text{X}^1\Sigma_g^+) \rightarrow \text{HCN}(\text{X}^1\Sigma^+) + \text{N}(^4\text{S})$. II: The Intermediate Complex Region,
M. Riad Manaa and David R. Yarkony, *Chem. Phys. Lett.*, **188**, 352 (1992).
- †7. Theoretical Studies of Spin-Forbidden Radiationless Decay in Polyatomic Systems: Insights from Recently Developed Computational Methods
David R. Yarkony, *J. Amer. Chem. Soc.*, **114**, 5406, (1992)
- †8. On the Intersection of Potential Energy Surfaces in Charge Transfer Reactions: A Crossing Seam for Two States of the Same Symmetry in the Reaction $\text{H}^+ + \text{NO}(\text{X}^2\Pi) \rightarrow \text{H} + \text{NO}^+(\text{X}^1\Sigma^+)$
M. R. Manaa and D. R. Yarkony, *J. Chem. Phys.*, **97**, 715 (1992).
9. Theoretical Studies of Spin-Forbidden Radiationless Decay in Polyatomic Systems II: Radiationless Decay of $\text{a-N}_2\text{O}_2$
Kiet A. Nguyen, Mark S. Gordon, John A. Montgomery, Jr., H. Harvey Michels and David R. Yarkony, *J. Chem. Phys.* (March 1993)

†Reprint included with this report.

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INTERACTIONS

The following invited talks were given by the principal investigator based on work performed during the course of this grant.

1. *The Electronic Structure Aspects of Spin-Forbidden and Electronically Nonadiabatic Processes*

presented at 1990 Gordon Conference on Atomic and Molecular Interactions
 Salve Regina Academy
 Newport, RI
 July 29-August 3, 1990

2. *Theoretical Studies of Electronic Energy Transfer: The Role of Allowed and Avoided Surface Crossings*

presented at Information Exchange Seminar on: Theoretical Approaches to Energy
 Transfer and Photochemical Processes
 Queen Kapioloani Hotel
 Honolulu, Hawaii
 December 27-30, 1990

3. *Theoretical Studies of Spin-Forbidden and Electronically Nonadiabatic Processes: Actual/Avoided Surface Crossings and Spin-Forbidden Radioless Decay in Dications*

presented at Proceedings of the High Energy Density Matter (HEDM) Conference
 Albuquerque Marriot Hotel
 Albuquerque, NM
 February 24-27, 1991

4. *Theoretical Studies of Spin-Forbidden and Electronically Nonadiabatic Processes:*

presented at ACS Symposium: State-to-State Dynamics on Multiple Potential Energy
 Surfaces
 Sheraton Hotel
 San Francisco, CA
 April 5-10, 1992

5. *Electronic Structure and Dynamical Aspects of Non-Born-Oppenheimer Processes in the Adiabatic States Basis*

presented at 31st Sanibel Symposium: Non-Born-Oppenheimer Methods
 Ponce de Leon Resort and Conference Center
 St. Augustine, FL
 March 14-21, 1992

6. *Radiationless Decay of Energetic Materials*

presented at Proceedings of the High Energy Density Matter (HEDM) Conference
 Antelope Valley Inn and Conference Center
 Lancaster, CA
 April 12-15, 1992